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Optimization Studies for Extraction of Copper from Rocks

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Abstract

This study investigates the optimization of quantitative analysis and extraction of copper from rocks in Oman. The focus is on enhancing the efficiency and accuracy of these processes for sustainable mining operations. The research employs Response Surface Methodology (RSM) to identify the optimal conditions for extracting copper using phosphoric acid boiling and thermite mixture methods. X-Ray Diffraction (XRD) is employed to characterize the extracted samples and understand the mineralogical compositions. The RSM analysis revealed the optimal conditions for copper extraction using phosphoric acid boiling. X-ray diffraction analysis of the extracted copper samples showed that the majority of the copper was extracted as metallic Copper (Cu). The optimization of these processes is crucial for improving the efficiency and sustainability of mining operations in the country. X-ray diffraction analysis provides valuable insights into the mineralogical composition of the extracted samples, which can be used to optimize the extraction processes further.

Keywords: *Copper, ICPAES, Mining, Optimization, RSM, XRD*

1.0 Introduction

Mining in Oman has a rich history that dates back thousands of years. The Sultanate of Oman has been known for its mineral resources and has played a significant role in the global mining industry[1]. The mining sector in Oman has witnessed various developments and has contributed to the country's economic growth and diversification. According to historical records, mining activities in Oman can be traced back to around 3,000 years ago. Miners from a region known as "Magan" were involved in the extraction and processing of copper ore. The copper ore was then exported via Bahrain to Sumer, an ancient civilization in Mesopotamia[2]. In recent history, Oman's mining industry experienced significant growth in the early 1980s[3]. Chromite ores became a significant focus of mining activities, and Oman started mining and exporting chromite ores during this period. Chromite ores were in high demand internationally, contributing to the economic development of the country[4]. Over the years, the government of Oman has recognized the mining sector's importance and has taken initiatives to promote and develop the industry. The Public Authority for Mining in Oman has been instrumental in creating a favourable environment for mining investments and providing support to mining companies. These efforts have attracted both domestic and foreign investments, leading to further advancements in the mining sector. The mining industry in Oman encompasses various minerals, including copper, chromite, limestone, gypsum, and marble. These minerals have been extracted and utilized in various industries, such as construction, manufacturing, and infrastructure development[1]. The mining sector has contributed significantly to Oman's GDP and has played a vital role in the country's economic diversification. The extraction of valuable minerals from

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rocks plays a crucial role in various industries, including mining and metallurgy. In the context of Oman, a country known for its rich mineral resources, the optimization of quantitative analysis and extraction processes for copper from rocks holds significant importance. This report aims to provide a detailed analysis of optimization studies conducted on the quantitative analysis and extraction of copper and quartz from rocks in Oman. Copper, a valuable metal mineral, has numerous industrial applications due to its excellent electrical conductivity and corrosion resistance[5]. The extraction of copper from rocks in Oman has the potential to contribute to the country's economic growth and development. The optimization studies in this research focus on enhancing the efficiency and accuracy of quantitative analysis and extraction processes of copper[6]. By studying the copper contents in rocks and evaluating the feasibility of mining operations, researchers aim to identify the most effective techniques and parameters for extraction. One of the key objectives of this research is to determine the optimal amount of phosphoric acid used, reaction time, and temperature for the extraction process. These parameters play a crucial role in influencing the extraction efficiency and yield of copper from rocks[5]. By optimizing these parameters, researchers aim to maximize the extraction efficiency while minimizing resource consumption and environmental impact. Furthermore, this research aims to investigate the relationship between XRD parameters, such as Pos. (°2θ), FWHM Left (°2θ), and d-spacing (Å), and the concentration of copper in the extracted samples. X-ray diffraction analysis valuable insights into the crystal structure and composition of materials, enabling researchers to estimate the copper concentration based on the XRD patterns[7]. The findings of this research will contribute to the existing knowledge on the optimization of quantitative analysis and extraction processes for copper from rocks in Oman. The results will provide valuable insights for the mining industry in Oman, aiding in the development of sustainable and efficient extraction practices.

2.0 Materials and Methods

The rocks which were used as raw material for the extraction process was collected from wilayat Al Suwaiq, a town in costal side of Oman and it is located in Al-Batinah region in the north east side of Oman. In order to analyze copper contents of the rocks, a well-known concentration solutions is prepared. Standard solution were prepared for copper analyzing in Atomic absorption spectrometer using solution of 2% HNO_3 which has concentration of 1000 mg/L. 100 ml solution of 100 mg/l prepared by adding 10 ml of standard solution of 1000 mg/l in a beaker than 90 ml distilled water added. Similarly, standard solutions were also prepared for analyzing silica quartz in Atomic absorption spectrometer using standard solution of 1000 mg/l. The volume required of the 1000 mg/l solution is 10 ml, as shown in the below table added to 90 ml distilled water for preparing solution of 100 mg/l. Using the same principle of dilution of high concentration solution, four different concentrations solutions were prepared of 2, 4, 6 and 8 mg/L concentrations to be used in atomic absorption spectroscopy. The crock samples were collected from various places in the Wilayat Al Suwaiq. The collected rocks were washed to remove any impurities and then left to dry. Once dry, they were crushed into small pieces manually using a hammer. The next step involved separating the different sizes of rock pieces. This was done by using a sieve mesh shaker, which separated the rocks based on size. From the separated pieces, two specific sizes, 300 mm and 150 mm, were taken for further use or analysis.

3.0 Experimental

3.1 Extraction of Copper

The extraction of copper metal was conducted using two distinct methods. In the first method, the rock samples containing copper is boiled in phosphoric acid. This process allowed for the separation and extraction of copper metal[8]. The second method involved burning the rock samples in a thermite mixture consisting of glycerol and potassium permanganate[9]. Through this method, the copper metal is also successfully extracted. These two methods provided different approaches to extracting copper metal, offering versatility in the extraction process.

3.2 Phosphoric Acid Boiling Method

In the Phosphorous acid boiling method, the first step involved weighing 80 grams of the copper and quartz rocks and transferring them into a 500 ml beaker. To remove any dust contamination, distilled water was added to the beaker, causing the dust to float at the top and be manually removed. The copper samples were then left in a drying oven for an entire day. After drying, any remaining dust on the samples was manually removed. The weight of the dried copper sample was 0.71 grams, and the weight of the dried quartz sample was 0.76 grams. Once the dust contamination was removed, 250 ml of 85% concentration phosphoric acid was added to each beaker containing the samples. The beaker with the copper sample was placed on a hotplate and heated at 325°C for 2 hours. Distilled water was added to the beaker during this process. After heating, the samples were left to cool down, resulting in the formation of a gel layer of acid around them. If the sample was boiled for too long, the acid would become thick and jelly-like. The beaker was then left to cool for 30 minutes, and the cover glass of the beaker was washed. The remaining phosphoric acid was poured off into an acid waste container. To ensure complete removal of dust and phosphoric acid, 500 ml of distilled water was added to the beaker once again. Additionally, 300 ml of distilled water and 50 ml of NaOH were added to the two beakers. The addition of sodium hydroxide solution was important for removing the silicates coating layer on the quartz grain. The beakers were covered using a glass dish and boiled for 10 minutes on a hotplate. After boiling, the beakers were lifted to cool down, and the sodium hydroxide solution was poured off into a waste container. The beakers were rinsed with 100 ml of distilled water. Finally, the samples were dried using an oven for an entire day.

3.3 Thermite Mixture with Glycerol and Potassium Permanganate

The use of Metallothermy (MT) and Self-propagating High-temperature Synthesis (SHS) is considered for processing different geological and technogenic materials. This method relied on an exothermic reaction to extract copper and quartz. In this process, 22.5 grams of rocks were mixed with 25 grams of aluminum and 30 grams of sulfur in powder form. The solid mixture was thoroughly mixed before being placed in a container on a hotplate for heating. A hole measuring 5 cm wide and 5 cm deep was created in the center of the solid thermite mixture, and potassium permanganate was added to fill the hole. Two pieces of 5 cm long magnesium ribbon were placed in the hole to facilitate ignition. Glycerol was used to ignite the highly oxidizing potassium permanganate. This combination is often used as an ignition source for thermite reactions. The reaction between these two is indeed exothermic, generating heat that initiates the thermite reaction. The ignition resulted in an exothermic reaction between potassium permanganate and glycerol, which can be represented by the equation:

$$14\,KMnO_4(s) + 4\,C_3H_5(OH)_3(l) \rightarrow 7\,K_2CO_3(s) + 7Mn_2O_3(s) + 5\,CO_2(g) + 16\,H_2O(g)$$

The reaction between potassium permanganate and glycerol resulted in the production of fire and heat, which was sufficient to ignite the two magnesium ribbons. These ignited the thermite mixture, causing a rapid combustion reaction. Copper extraction involves different processes depending on the ore type. Some methods involve leaching (dissolving copper compounds) or electrolysis (using electricity to separate copper from a solution). To calculate the percentage of copper extracted from the thermite reaction, the following formula was used:

$$\text{Copper \%} = \frac{\text{Weight of Copper extracted}}{\text{weight of rocks}} \times 100$$

The extracted solutions are characterized by XRD, and ICP-AES methods used to identify the nature and the concentration of the impurities removed by the gettering process.

3.4. X-Ray Diffraction (XRD)

The use of X-Ray Diffraction (XRD) in copper and quartz extraction is a crucial analytical technique. XRD enables the identification and characterization of crystalline phases present in copper[10,11]. By analyzing the diffraction patterns produced when X-rays interact with the crystal lattice, XRD can determine the composition and structure of the minerals. This information is vital for understanding the mineralogical composition of the ore and optimizing extraction processes[12,13]. The result obtained is verified with the calibrated values of copper as shown in the Figure 1.

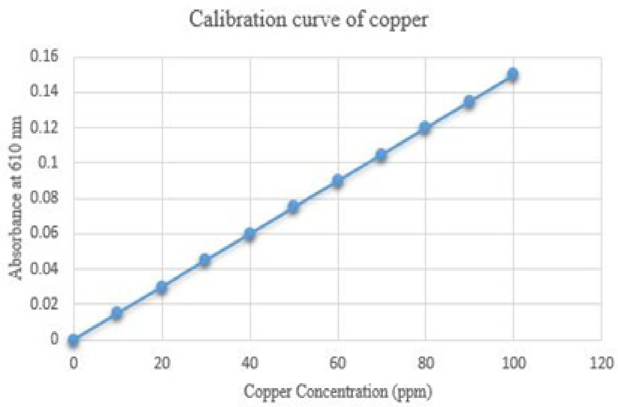

Figure 1. Calibration curve of copper.

4.0 Results

The XRD image for copper sample number R2-2 is shown in Figure 2. The presence of a variety of copper oxides is observed. The most intense peak is at around 35.5° 2θ, which corresponds to the (002) plane of cuprite (Cu_2O). The presence of multiple copper oxides in the sample suggests that it has been exposed to oxidizing conditions. This could be due to weathering or to the use of oxidizing agents during the extraction process. Based on the peak intensities[14], it is estimated that the sample is primarily composed of cuprite, with smaller amounts of tenorite, paratacamite, and atacamite. The presence of a variety of copper oxides. The most intense peak is at around

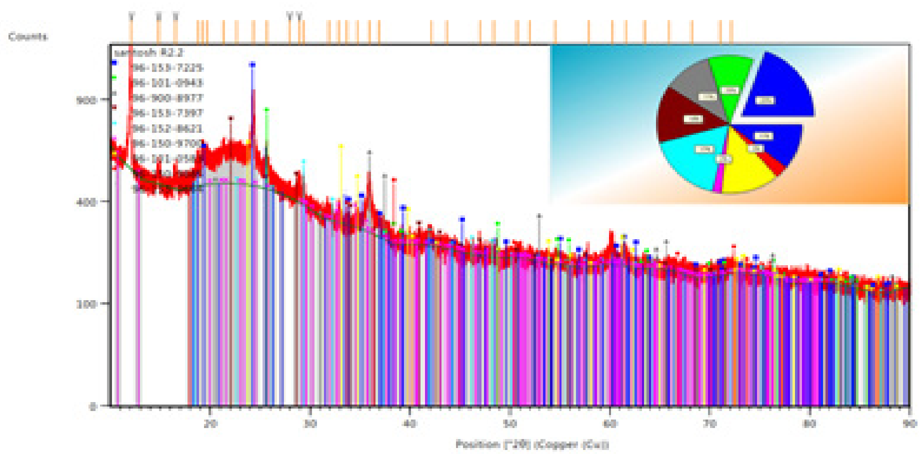

Figure 2. X-ray diffraction pattern of position 2θ vs count for copper (Sample R2-2).

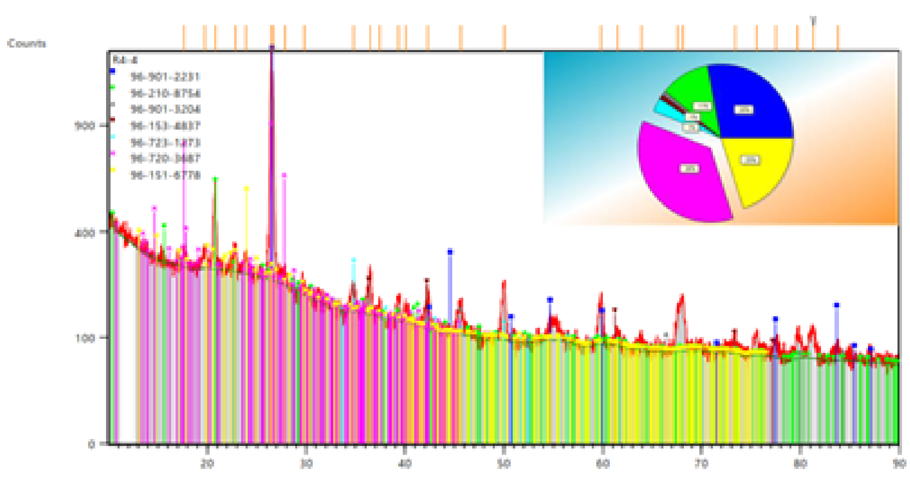

Figure 3. X-ray diffraction pattern of Position 2θ vs Count for copper (Sample R4-4).

35.5° 2θ, which corresponds to the (002) plane of cuprite (Cu_2O).

The presence of multiple copper oxides in the sample suggests that it has been exposed to oxidizing conditions[15,16]. This could be due to weathering or to the use of oxidizing agents during the extraction process.

Figure 3 shows the XRD image for copper sample number R4-4 shows a strong peak at around 43.3° 2θ, which corresponds to the (111) plane of copper. This indicates that the sample is highly crystalline copper. The FWHM of the peak is relatively narrow, suggesting that the crystallite size is relatively large. In addition to the (111) peak, the XRD image also shows weaker peaks at around 50.5° 2θ and 74.2° 2θ, which correspond to the (200) and (220) planes of copper, respectively. These peaks are typically less intense than the (111) peak because they correspond to higher energy diffraction planes. Overall, the XRD image for copper sample R4-4 indicates that the sample is highly crystalline copper with a relatively large crystallite size.

5.0 Discussion

5.1 Statistical Analysis

The optimal conditions for extracting copper and silica were statistically determined using the Response Surface Methodology (RSM). Researchers used Design Expert software to analyze data collected through the Central Composite Design, allowing them to assess the mathematical relationship between the dependent and independent variables. Based on the values obtained from the ANOVA quadratic model given in Table 1, various factors and their interactions on the copper extraction process are significantly analyzed:

Phosphoric acid (A): This factor has a highly significant effect on copper extraction with a p-value < 0.0001. This indicates that increasing the concentration of phosphoric acid has a positive impact on extraction efficiency.

Temperature (B): Temperature shows a less significant effect with a p-value of 0.1312. While it may not be as

Table 1. ANOVA for the quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	704.77	9	78.31	7.09	0.0026
A-Phosphoric acid	439.70	1	439.70	39.81	< 0.0001
B-Temp	29.86	1	29.86	2.70	0.1312
C-Time	58.18	1	58.18	5.27	0.0446
AB	16.70	1	16.70	1.51	0.2469
AC	11.52	1	11.52	1.04	0.3312
BC	0.4325	1	0.4325	0.0391	0.8471
A^2	52.88	1	52.88	4.79	0.0535
B^2	17.60	1	17.60	1.59	0.2355
C^2	4.86	1	4.86	0.4404	0.5219
Residual	110.46	10	11.05		
Lack of Fit	16.35	5	3.27	0.1737	0.9613
Pure Error	94.11	5	18.82		
Cor Total	815.23	19			

impactful as phosphoric acid, it still suggests some influence on the extraction process.

Time (C): Similar to temperature, time has a moderate effect on copper extraction with a p-value of 0.0446. Increasing the leaching time can potentially enhance copper recovery

Analysis of Run Number vs. Residual Values of copper extraction based on the final equation in terms of coded factors.

Final equation in terms of coded factors:

Residuals = 83.94+ 6.63A + 1.73B + 2.41C -1.44AB +1.20 AC + 0.2325 BC -4.38 A^2 -2.53 B^2 + 1.33 C^2

Final equation in terms of actual factors:

Residuals = -0.431+ 0.009 (Phosphoric acid) + 0.016 (Temperature) - 0.00037 (Time) + 0.00063 (Phosphoric acid x Temp) + 0.000593 (Phosphoric acid x Time) +0.000115 (Temp x Time) - 0.002165 (Phosphoric acid^2) - 0.001249 (Temp^2) + 0.000657 (Time^2)

The analysis of the final equation in terms of coded and actual factors and the run number vs. residual values plot suggests that the model adequately captures the variability in the data and that there is a positive correlation between the residuals and both pressure and temperature. However, the relationship between the residuals and these factors shown in Figure 4. Is non-linear, meaning that the rate of increase in residuals slows down at higher pressure and temperature values.

5.2 Optimization of the Process via RSM

The plot of externally scrutinized residuals versus normalized % probability of copper extraction as shown in Figure 5 Shows a generally linear relationship, with a slight positive slope. This indicates that the model is adequately capturing the variability in the data and that there is a slight positive correlation between the residuals and the normalized % probability of copper extraction.

The fact that the slope is slightly positive suggests that the model may be underestimating the copper extraction at higher normalized % probability values.

5.3 Response Surface Plots

The response surface plots of copper as shown in the Figure 6. Copper extraction efficiency increases with increasing phosphoric acid volume. This is because phosphoric acid dissolves the copper oxides and other minerals present in the ore, making the copper more accessible for extraction. Copper extraction efficiency increases with increasing temperature up to a certain point. Beyond this point, the extraction efficiency decreases. This is because the high temperature can lead to the formation of insoluble copper compounds. Here is a significant interaction between phosphoric acid and temperature. At high phosphoric acid volume, the effect of temperature on copper extraction efficiency is reduced. This is because the high phosphoric acid concentration already dissolves most of the copper oxides, and the additional increase in temperature does not have a significant impact on the extraction efficiency.

The 3D response surface plot is shown in the Figure 7 shows the relationship between copper recovery, phosphoric acid concentration, and time. The plot is

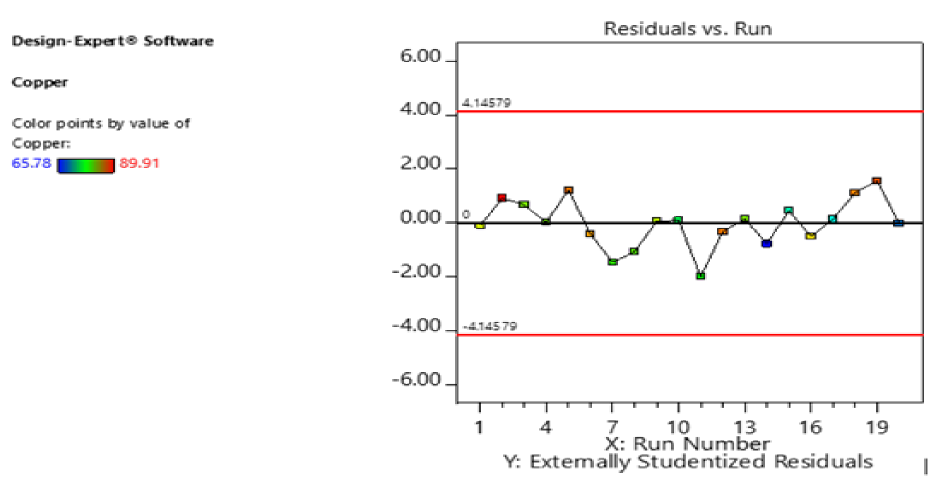

Figure 4. Plot of residuals vs runs for copper.

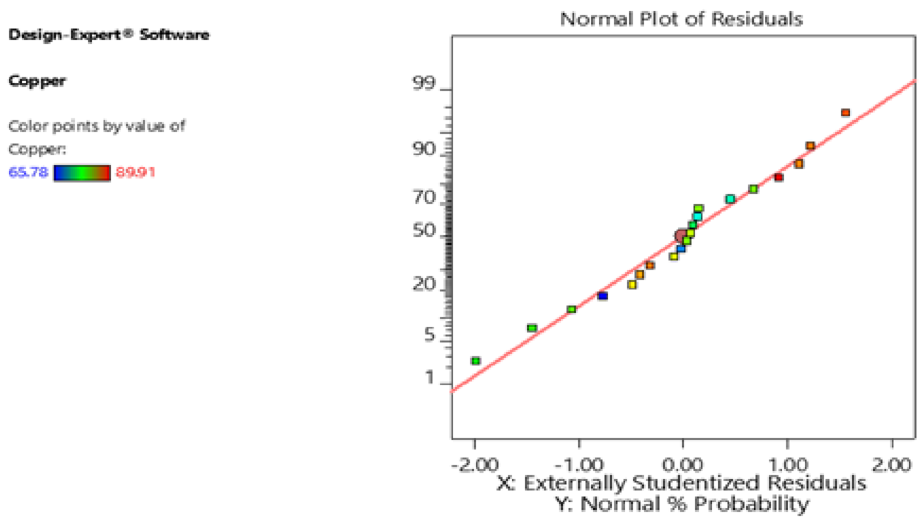

Figure 5. Plot of externally scrutinized residuals versus normalized % probability.

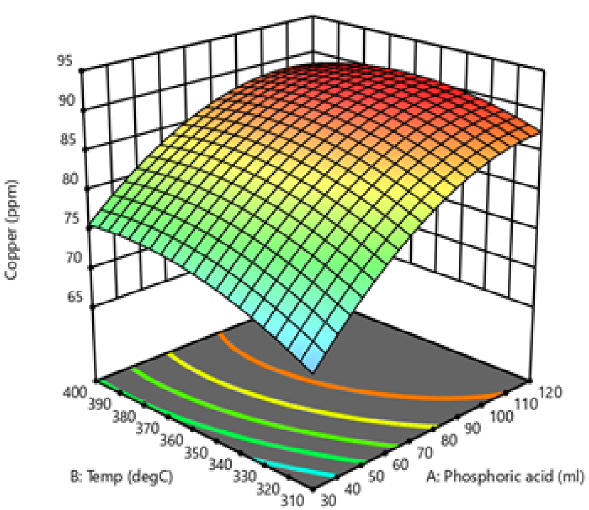

Figure 6. 3D response surface plots on the effects of process variables such as phosphoric acid and temperature on copper recovery.

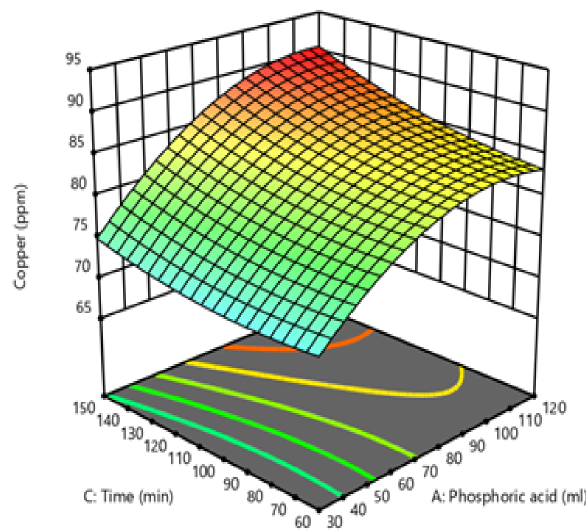

Figure 7. 3D response surface plots on the effects of process variables such as phosphoric acid and time on copper recovery.

asymmetrical, indicating that the effect of phosphoric acid on copper recovery is more pronounced than the effect of time. The plot shows that copper recovery increases with increasing phosphoric acid concentration and time, up to a certain point. Beyond this point, the copper recovery decreases. This is because high phosphoric acid concentrations and long leaching times can lead to the formation of insoluble copper compounds.

The plot of predicted versus actual values for copper recovery is shown in Figure 8 shows a good correlation between the predicted and experimental values, with a coefficient of correlation (R^2) of 0.95. This indicates that the model is able to accurately predict the copper recovery given the input variables. However, it is important to note that the plot also shows a slight bias, with the predicted values being consistently higher than the experimental

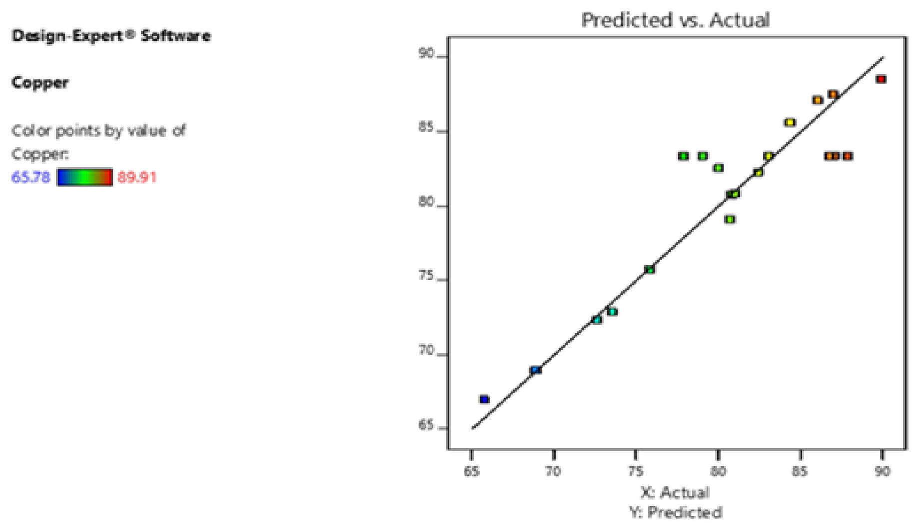

Figure 8. 3D response surface plots on the effects of process variables such as phosphoric acid and temp copper recovery.

values. This suggests that the model may be overestimating the copper recovery.

One possible explanation for this bias is that the model does not fully capture the non-linear relationship between the input variables and the copper recovery. Another possibility is that there are some other factors that influence copper recovery that are not being accounted for in the model. Overall, the plot of predicted versus experimental values for copper recovery suggests that the model is able to accurately predict the copper recovery, but there is a slight bias towards overestimating the recovery. Further investigation is needed to identify the cause of this bias and to improve the accuracy of the model.

6.0 Conclusion

This research investigated the optimization of quantitative analysis and extraction processes for copper from rocks in Oman. Phosphoric acid concentration significantly influences both copper and quartz extraction. Increasing phosphoric acid concentration enhances extraction efficiency, but high concentrations can lead to the formation of insoluble copper compounds. While not as impactful as phosphoric acid, temperature can influence the extraction process, with an optimal range for maximizing efficiency. Longer leaching times can enhance copper recovery, but excessive time can also lead to the formation of insoluble compounds. Response surface plots and contour plots provide valuable insights into the interactions between process variables

7.0 Author Contributions

The study was conceptualized by Santosh Walke, who also developed the methodology. Varghese M J contributed the software, while Santosh Walke performed validation alongside Manahil Al Khusaibi. Formal analysis and investigation were conducted by Abeer Al Saadi and Manahil Al Khusaibi, while Santosh Walke drafted the manuscript and all authors participated in its review and editing. Visualization was a collaborative effort, and Santosh Walke provided supervision and managed the project administration. Finally, funding was acquired by Santosh Walke. All authors have read and agreed to the published version of this manuscript.

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